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14. ABSTRACT

Using the dicyanate ester of bisphenol E (also known as Primaset LECy), we have illustrated the difficulties inherent in measurement of the glass transition temperature of this high-temperature thermosetting polymer via dynamic mechanical analysis alone. These difficulties result from the residual cure of samples heated beyond their glass transition temperatures. Comparative DSC and oscillatory TMA studies carried out using a variety of cure conditions showed that simply increasing the heating rate did not suppress the residual cure, although in many cases it allowed the glass transition to become apparent before the onset of rapid residual cure. The results indicated that ensuring the reliability of dynamic mechanical measurements of the glass transition temperature is very difficult to accomplish without the knowledge of residual cure properties provided by methods such as DSC.

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Effect of In-Situ Cure on Measurement of Glass Transition Temperatures in High-Temperature Thermosetting Polymers

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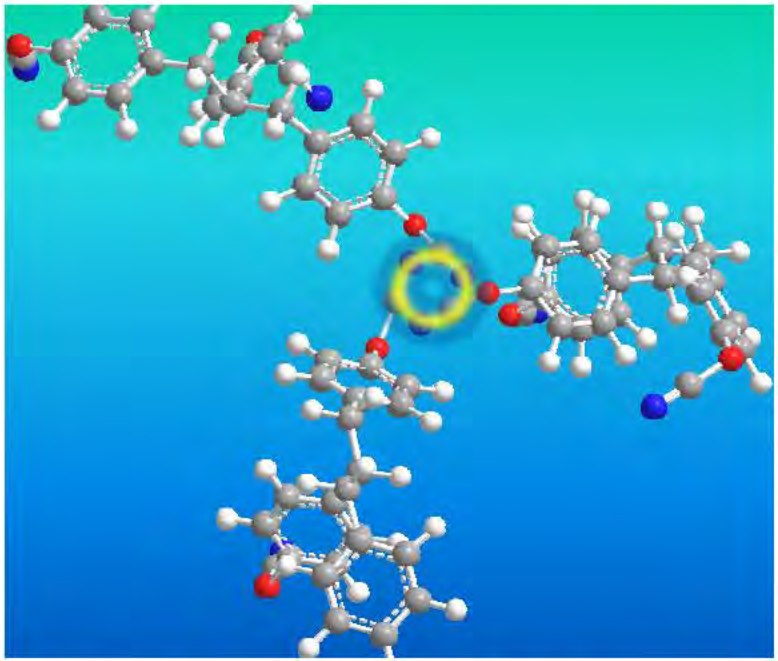
20 May 2015

Outline: The Effects of "Frozen" Chemistry

- Background: Importance of Conversion
- Progress in Conversion Measurement
- Difficulties in Glass Transition Temperature Measurement
- Solutions that Work (and Some that Do Not Work)

Acknowledgement: Air Force Office of Scientific Research; AMG Group Members

Model High-Temperature Thermosetting Polymers: Cyanate Esters



Principal reaction:
3 OCN ->
Selectivity: 80% - > 98%
ΔH_f = - 110 kJ / eq.
Conversion kinetics; Auto-catalytic (may be catalyzed)
Typical conversion rate: ~50%/hr (max) at 250 °C (uncatalyzed)
Extend of conversion: Limited to T_G = T_{cure} + 30-60 °C

- A single, known reaction predominates.
- Methods for assessing the extent of side reactions, and for minimizing side reactions, are known.
- The structure of even fully cured networks is easily analyzed and described quantitatively.
- Samples are easy to prepare in the laboratory; cure conditions are readily manipulated over a very wide range of rates.

Cyanate Esters: Next-Generation High-Performance Composite Resin

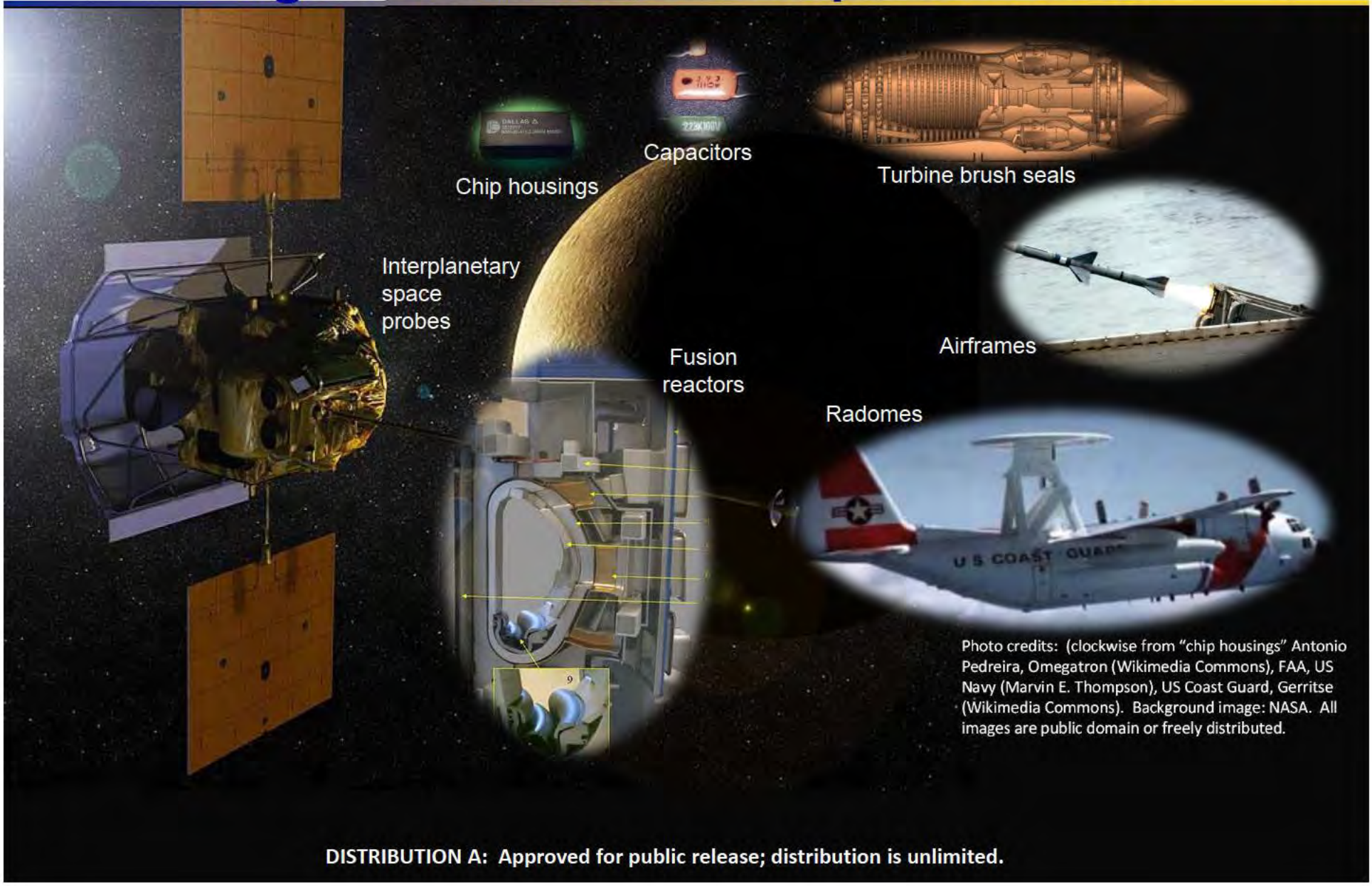
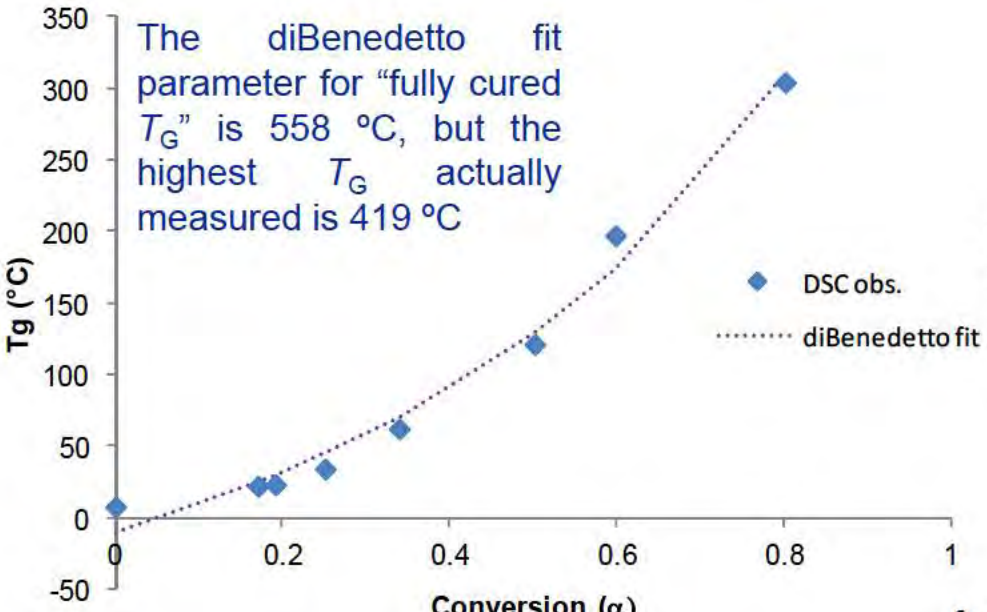
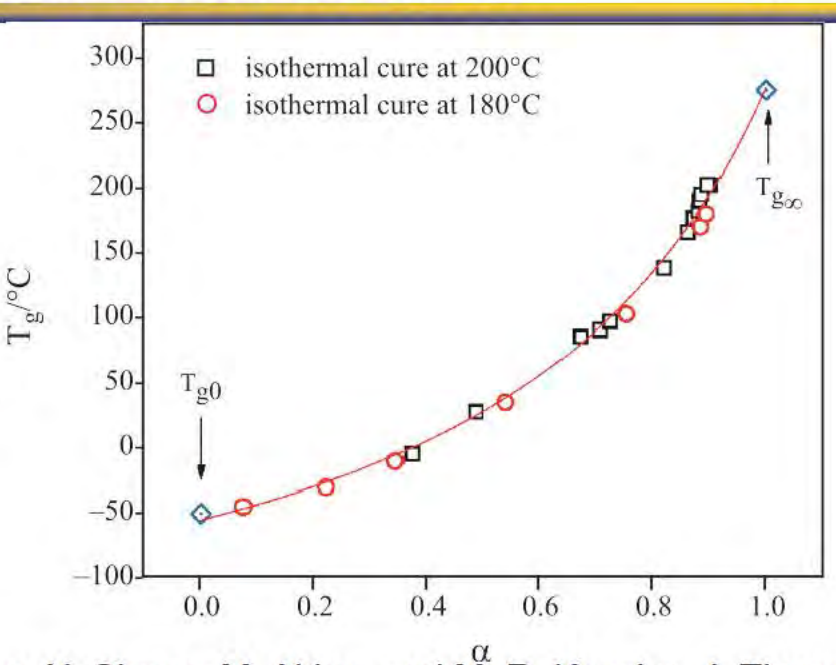


Photo credits: (clockwise from "chip housings" Antonio Pedreira, Omegatron (Wikimedia Commons), FAA, US Navy (Marvin E. Thompson), US Coast Guard, Gerritse (Wikimedia Commons). Background image: NASA. All images are public domain or freely distributed.

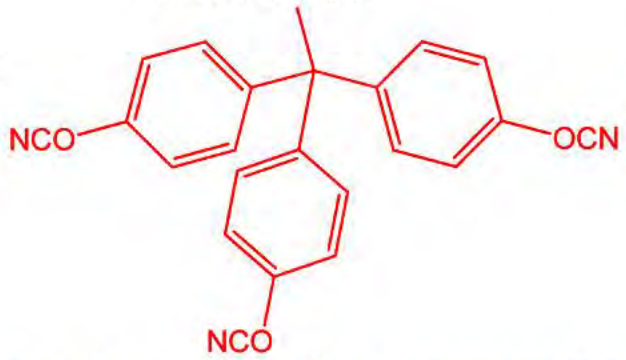
Cyanate Ester Networks: Defined by Composition and Conversion



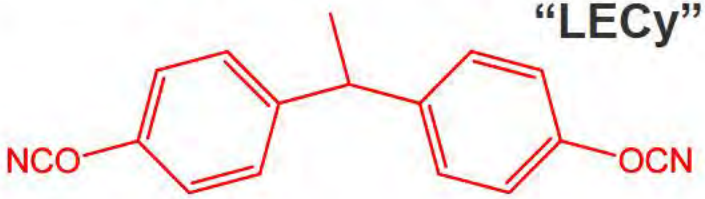


from X. Sheng, M. Akinc, and M. R. Kessler, *J. Therm. Anal. Calorim.* **2008**, *93*, 77-85 for EX-1510

"ESR255"

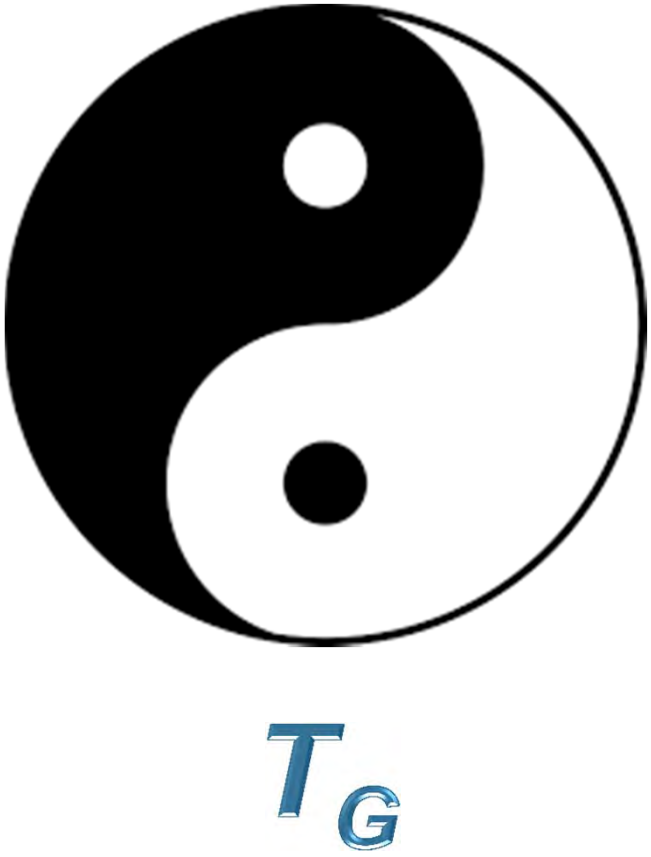


"LECy"



- In addition to glass transition temperature, many properties, such as density and water uptake, are mainly functions of conversion and monomer type.

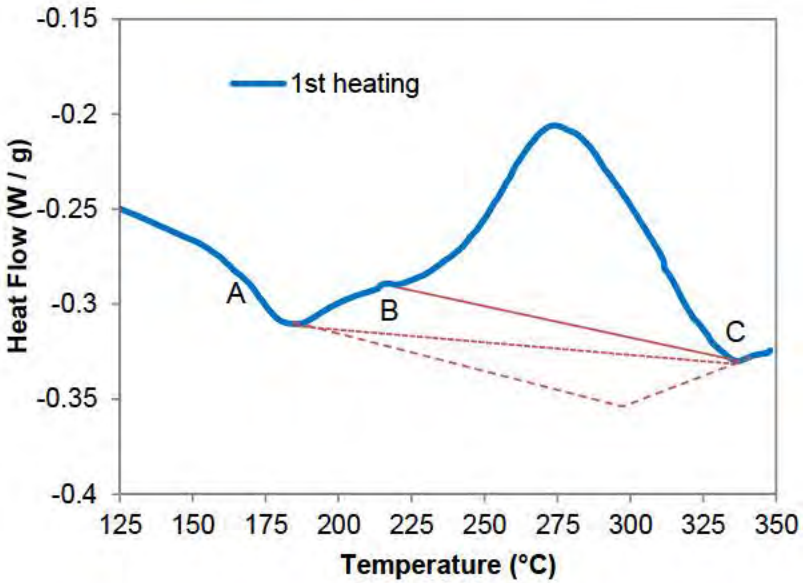
Conversion and T_G Are Intrinsically Linked in Cyanate Esters



- Under non-degrading conditions (T < 300 °C), if conversion changes, then the T_G must also change with it. If the T_G changes, then cure has occurred. The only observed changes should be increases over time!
- A measurement of conversion is a measurement of T_G. Measurements of conversion and T_G may be combined to yield a more precise estimate of both parameters.
- Any measurement that indicates a change in conversion, such as non-reversible heat flow in a DSC experiment, also measures the rate of change of T_G.
- The preceding statements are true for any thermosetting network that forms by a single reaction method and is not subject to degradation during measurement.

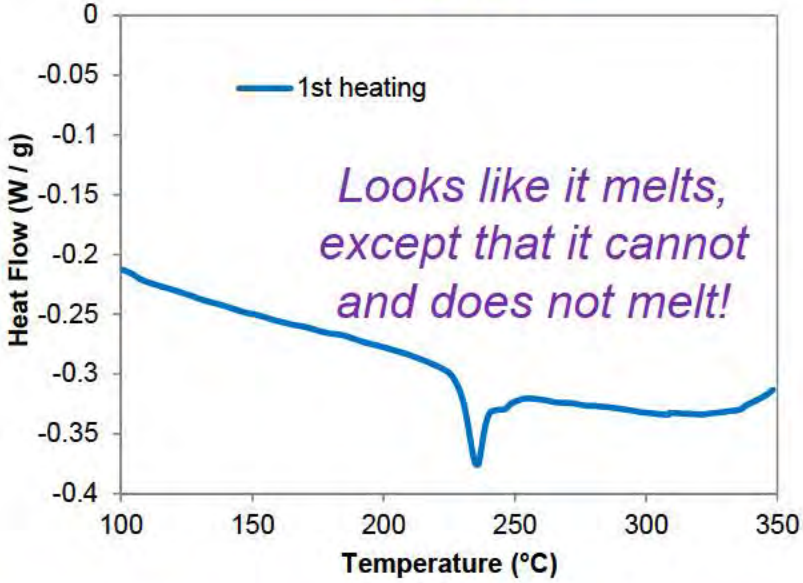
Conversion by DSC: The Usual Way

Typical Residual Cure



Even in samples with well-defined exotherms, there is ambiguity …

What about this case?

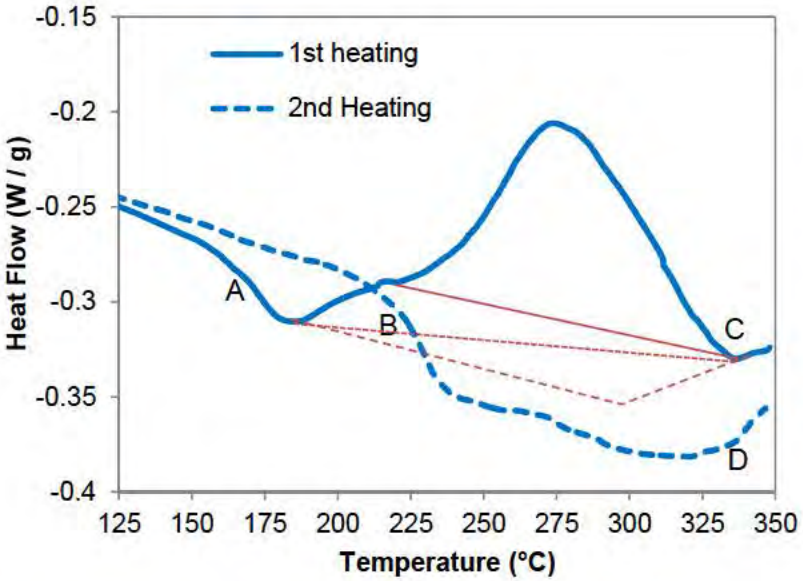


At high conversions, the typical approaches become impossible

- Current solution: live with absolute error of up to 0.05 in conversion by DSC, corresponding to predicted T_G uncertainty of 25 – 50 °C.

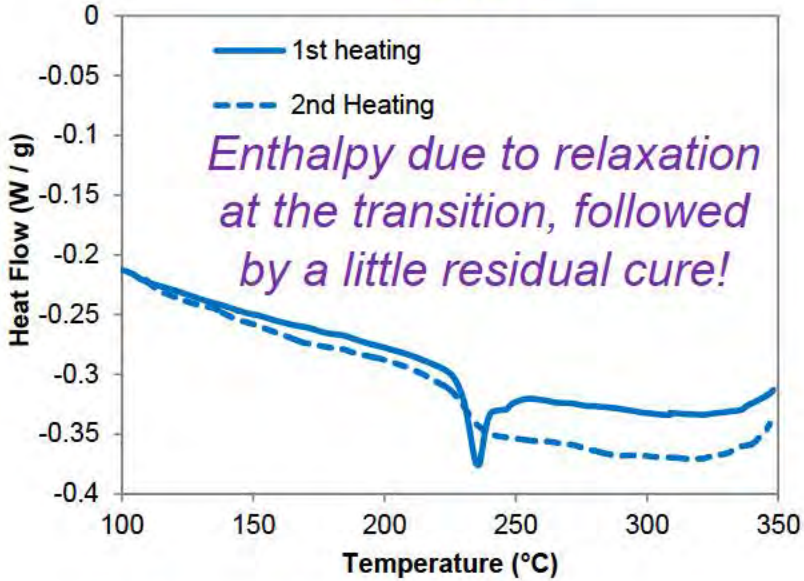
Re-Scanning Shows the Limitations of Typical Baseline Approach

Typical Residual Cure



Re-scanning shows us where the baseline is above T_G , how T_G shifts, how T_G is partly hidden, and where instability starts

What about this case?

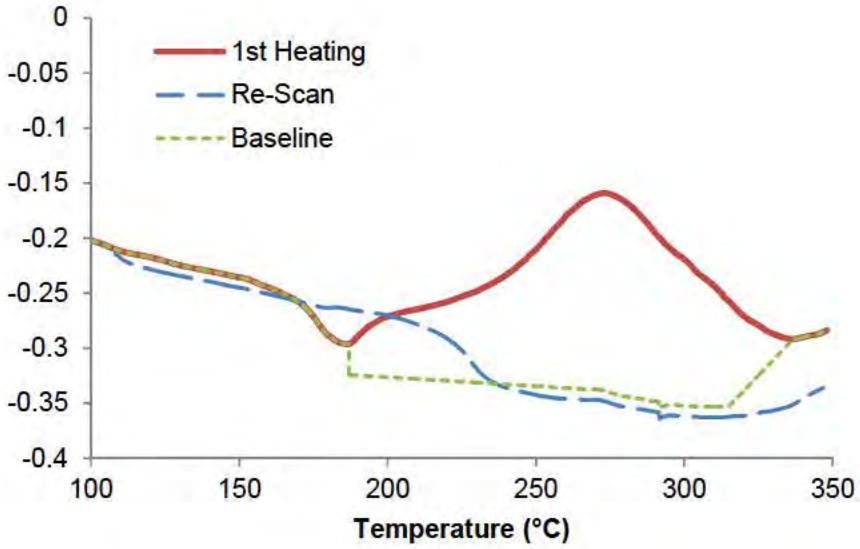


… and it works at high conversions

- Better solution: use the re-scan as a baseline (Kessler group).

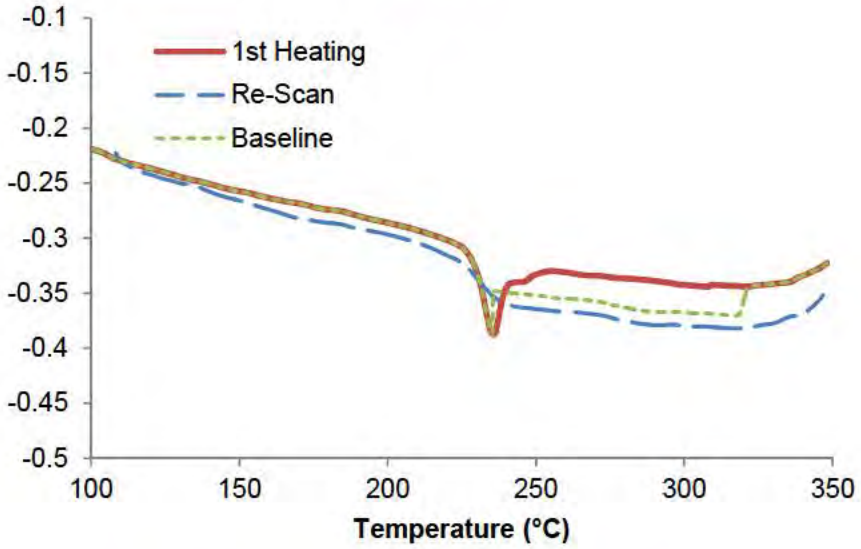
Building a Baseline from Re-Scanning

Typical Residual Cure



Magnitudes of step change should match (roughly), shift in step change should fit diBenedetto equation

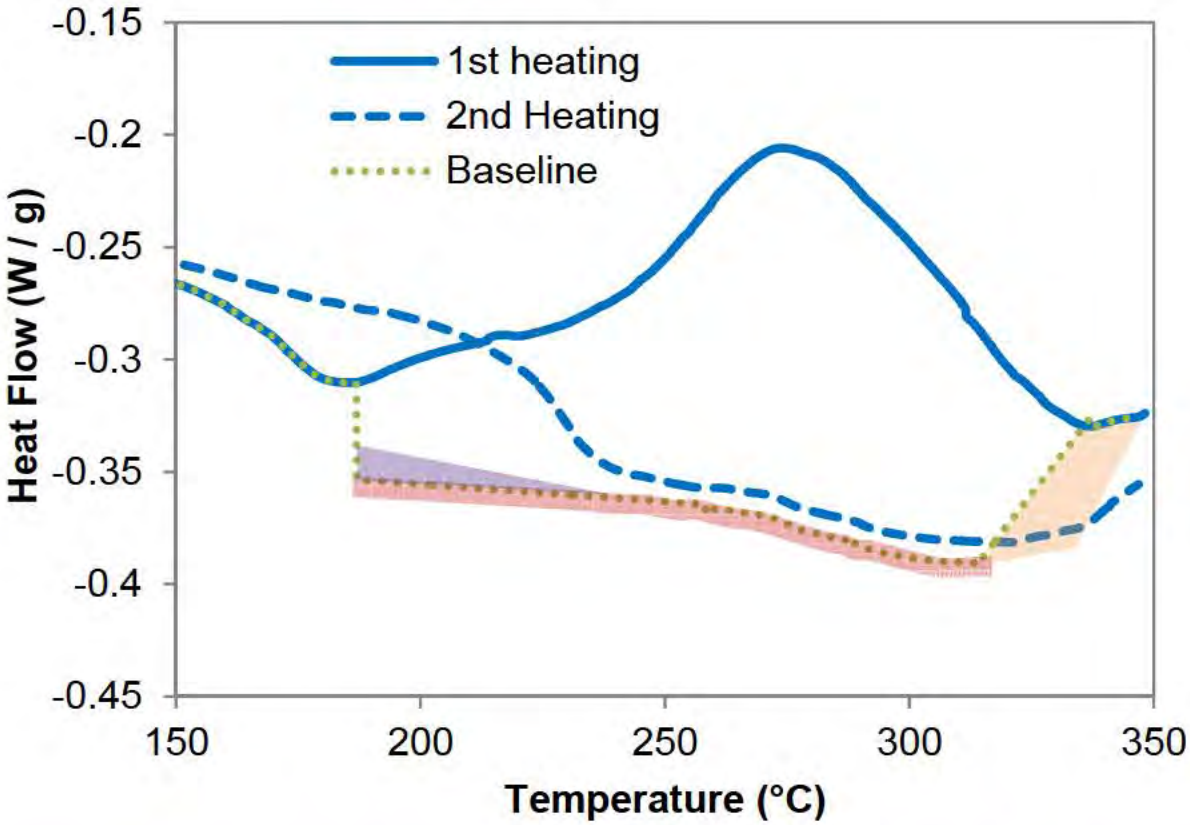
What about this case?



… and the exact same algorithm works well with samples at high conversion

- Even better solution: use the re-scan + account for shift in T_G & instability (our idea).

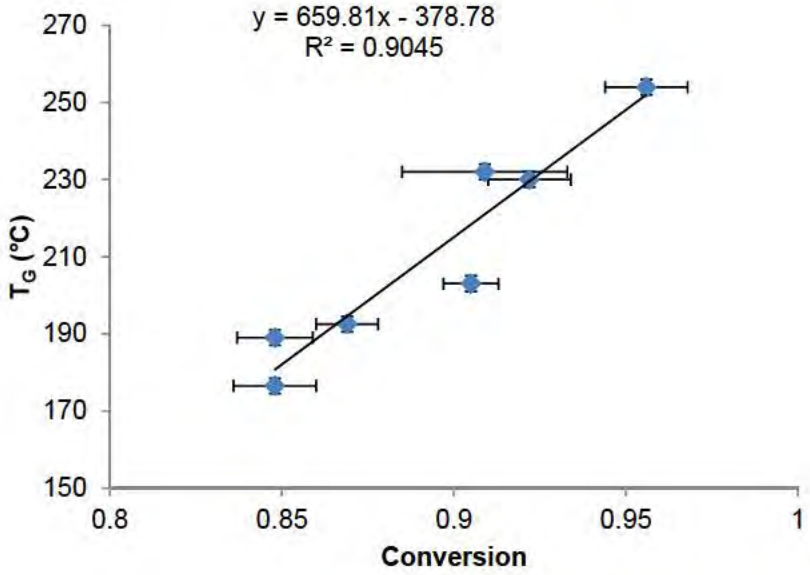
Estimating Uncertainties



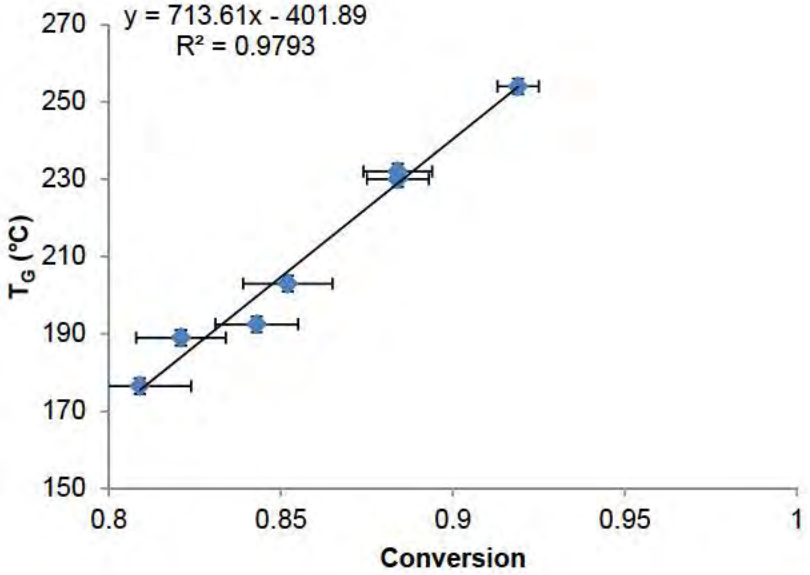
- Uses – range of possible offset values (light red); range of possible instability corrections (orange); estimated error in slope of extrapolation in re-scan using 0.05 W/g expected size of step change (purple). These errors are assumed to be uncorrelated.

Assessment of New Baseline Method

Old Way: Re-scan with range of possible offsets = baseline



New Way

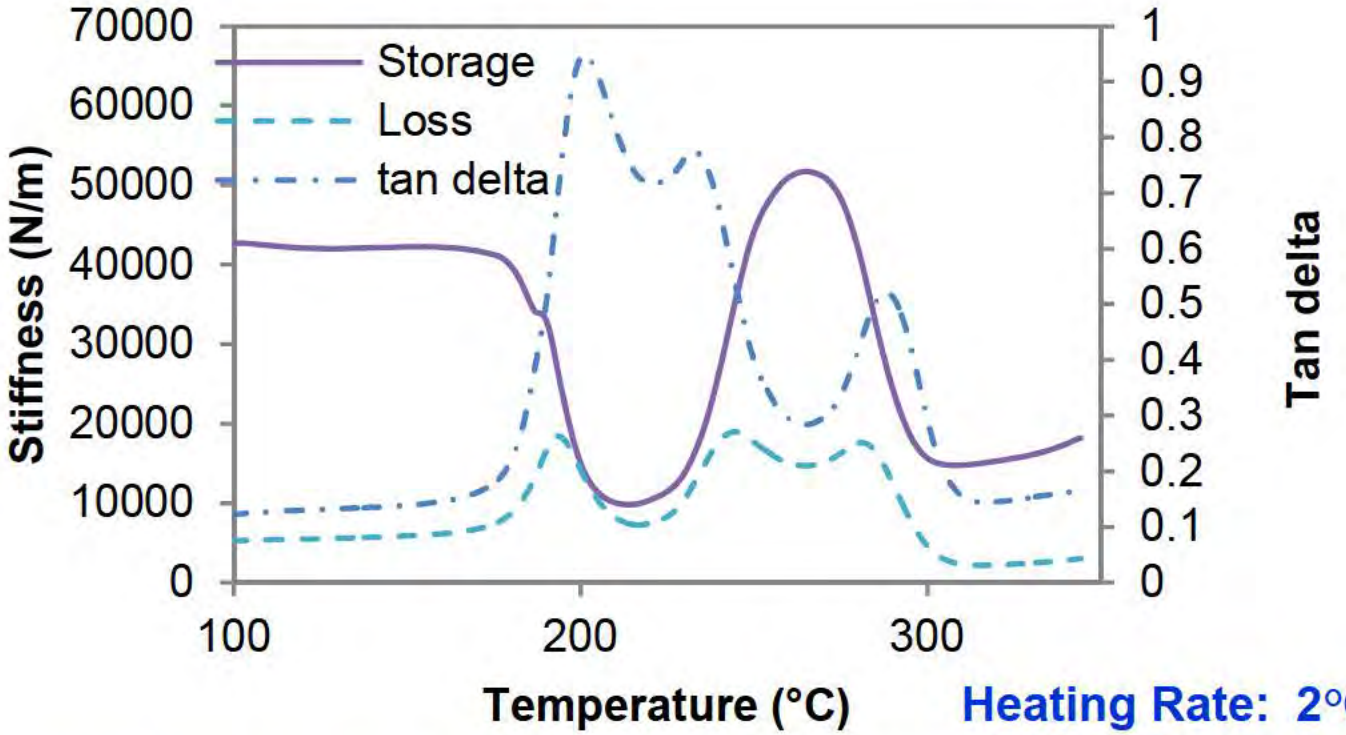


- Uncatalyzed LECy with cure at 170 °C / 24 hr + post-cure from none to 240 °C for 1 hr.
- Old way predicts glass transition temp at full cure = 282 °C; new method predicts 312 °C, experiments show it is at least 304 °C .

"Direct" Measurement of T_G?

LECy, catalyzed with 2 phr nonylphenol + 160 ppm Cu as Cu(II)Acac

Cured at 150 °C for 12 hours



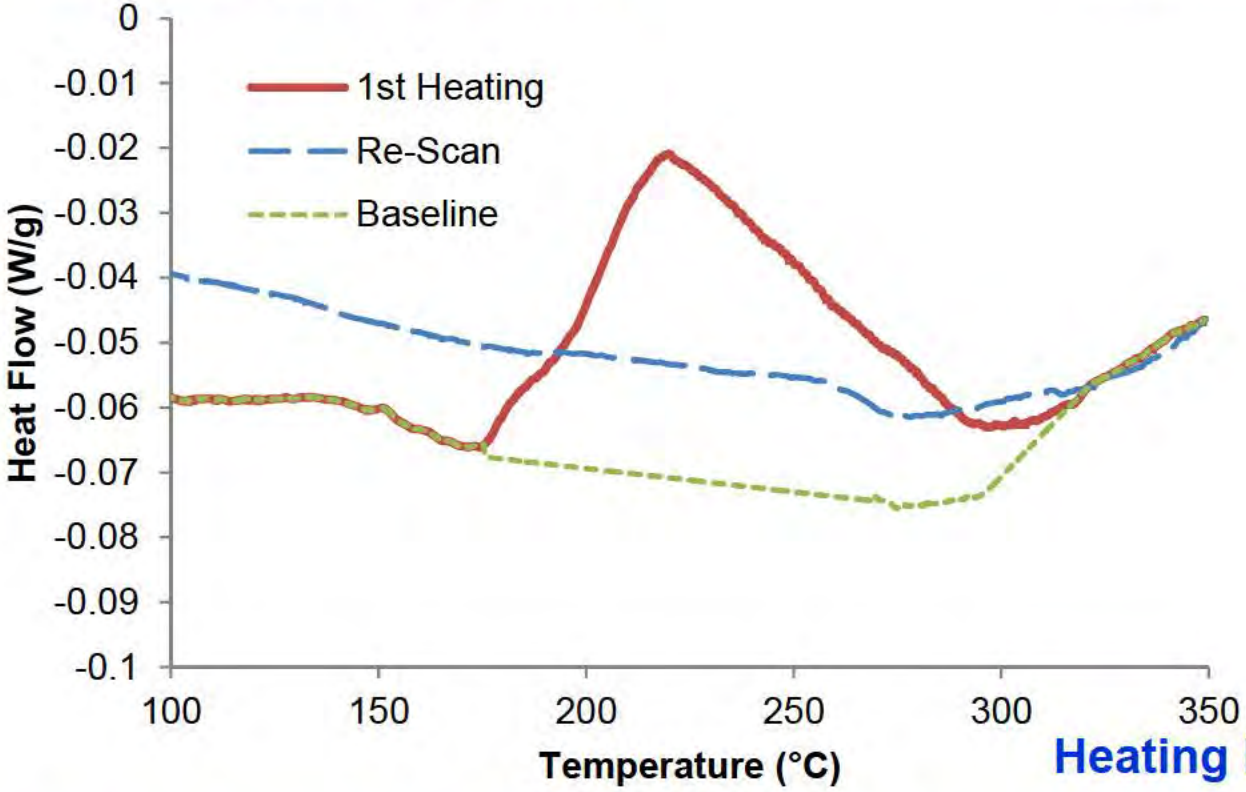
Heating Rate: 2°C / min.

- Oscillatory TMA done in accordance with typical procedure shows three peaks for this single-component system, one peak corresponds to an increase of stiffness.

Corresponding DSC Trace

LECy, catalyzed with 2 phr nonylphenol + 160 ppm Cu as Cu(II)Acac

Cured at 150 °C for 12 hours



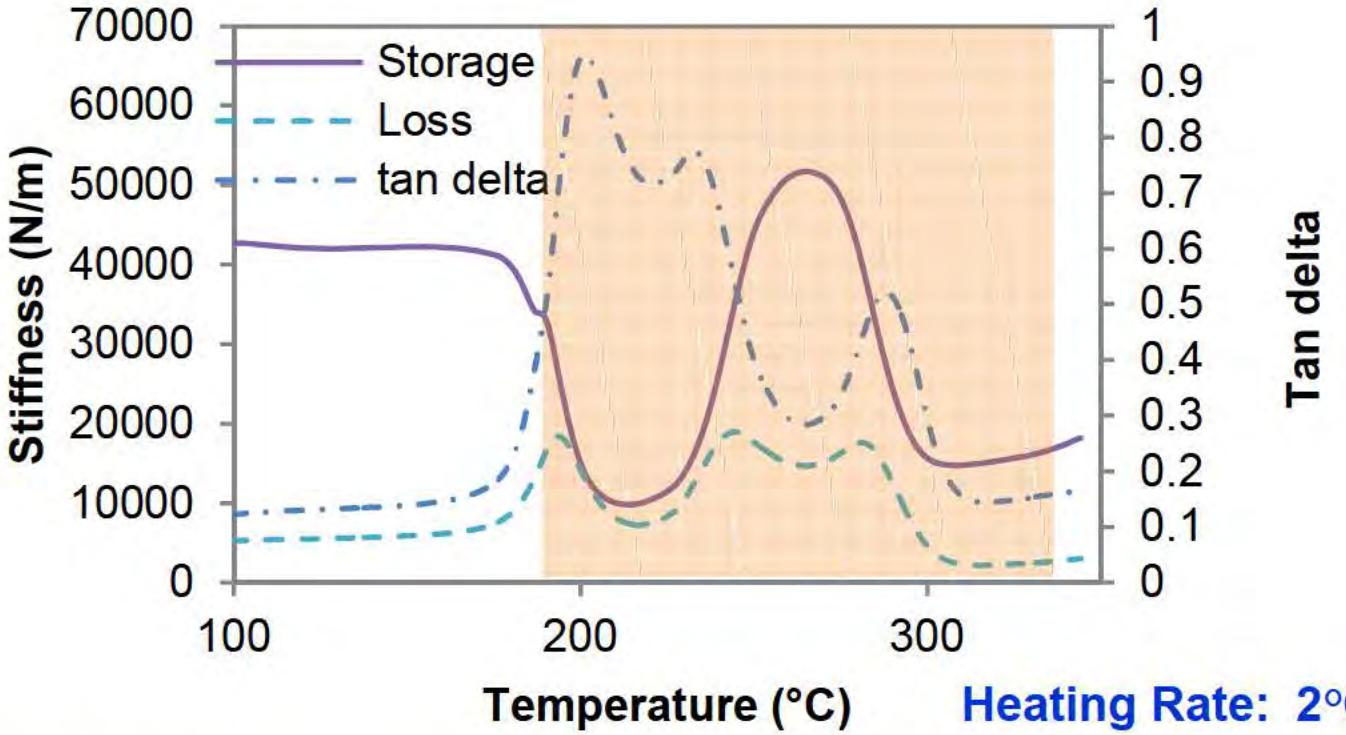
Heating Rate: 2°C / min.

- Excess heat release above 175 °C indicates that the sample is undergoing cure.

"Direct" Measurement of T_G?

LECy, catalyzed with 2 phr nonylphenol + 160 ppm Cu as Cu(II)Acac

Cured at 150 °C for 12 hours



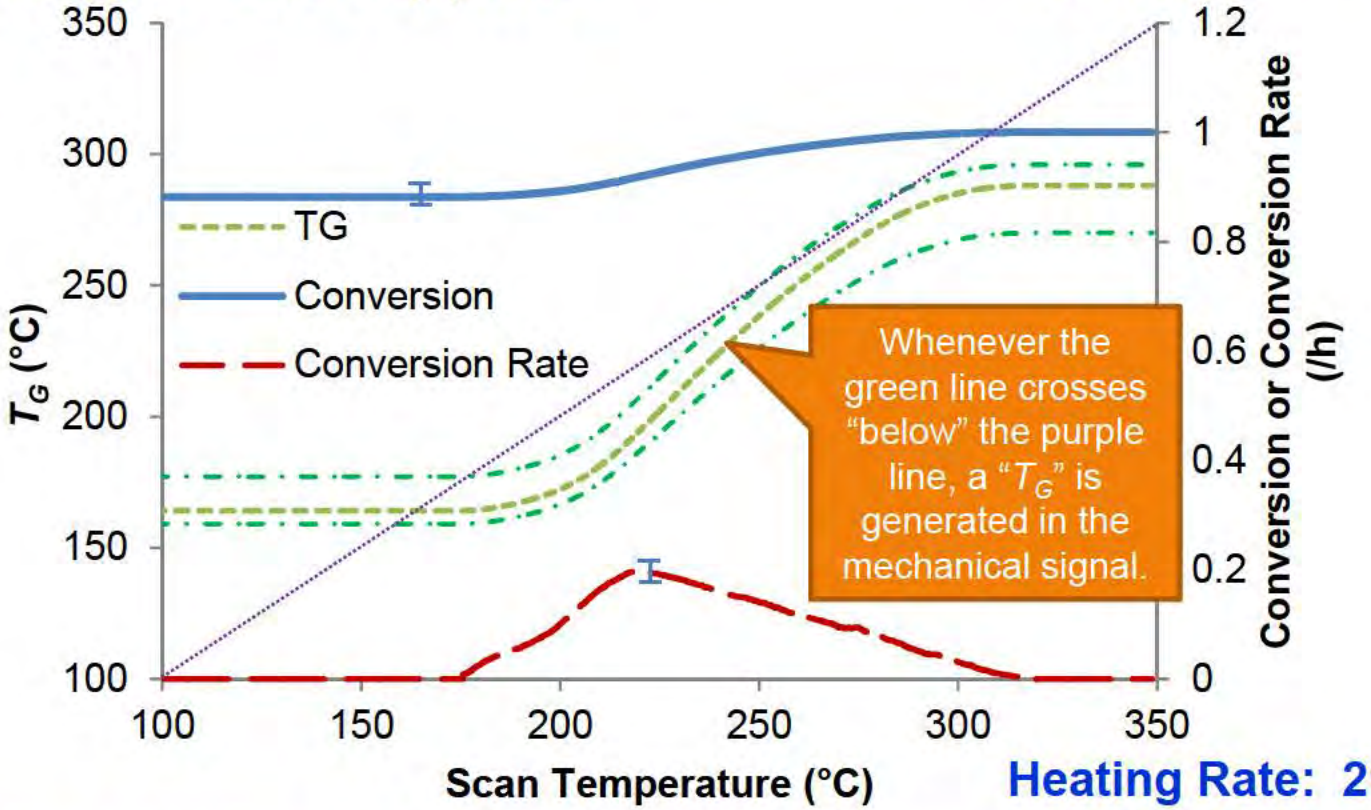
Heating Rate: 2°C / min.

- In the shaded region, the sample is undergoing cure, which means that the T_G is changing while an attempt is being made to measure it!

Inferred OTMA T_G from Conversion Measurements

LECy, catalyzed with 2 phr nonylphenol + 160 ppm Cu as Cu(II)Acac

Cured at 150 °C for 12 hours



Heating Rate: 2°C / min.

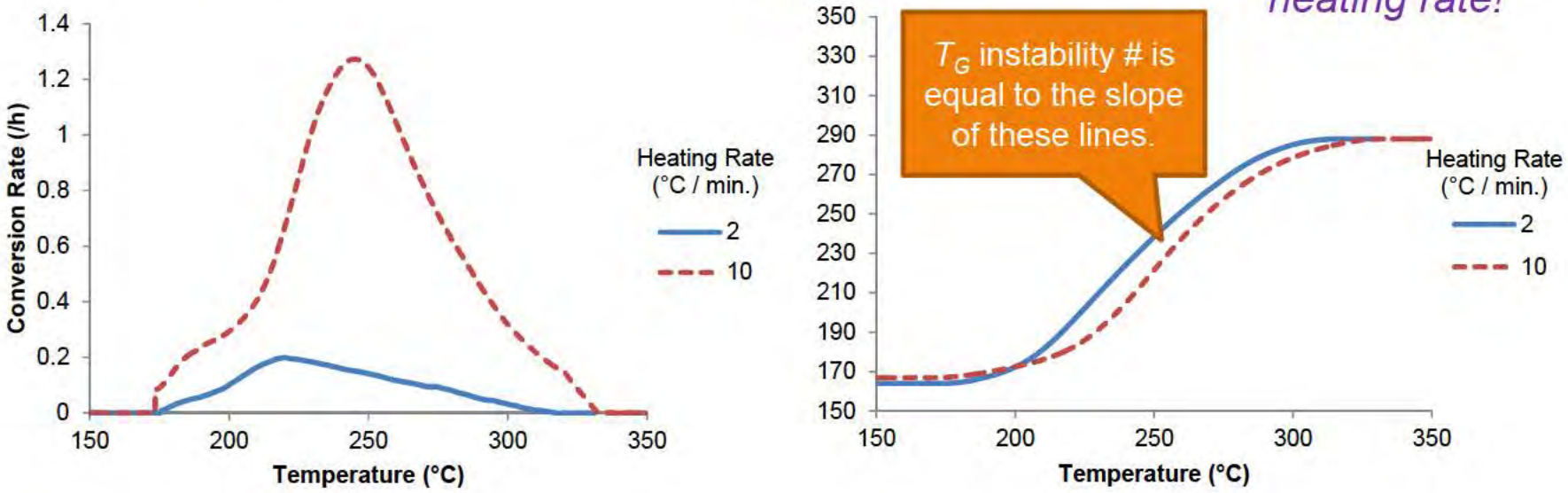
- The darker green lines indicate the uncertainty limits for T_G. Main sources of uncertainty are DSC to OTMA correspondence, and effect of degradation. Note that T_G increases faster than the scan temperature.

Why Not "Outrun" T_G?

T_G instability # =

$$\frac{\text{Sensitivity x Cure Rate}}{\text{Heating Rate}}$$

Turns out the cure rate tends to be proportional to the heating rate!

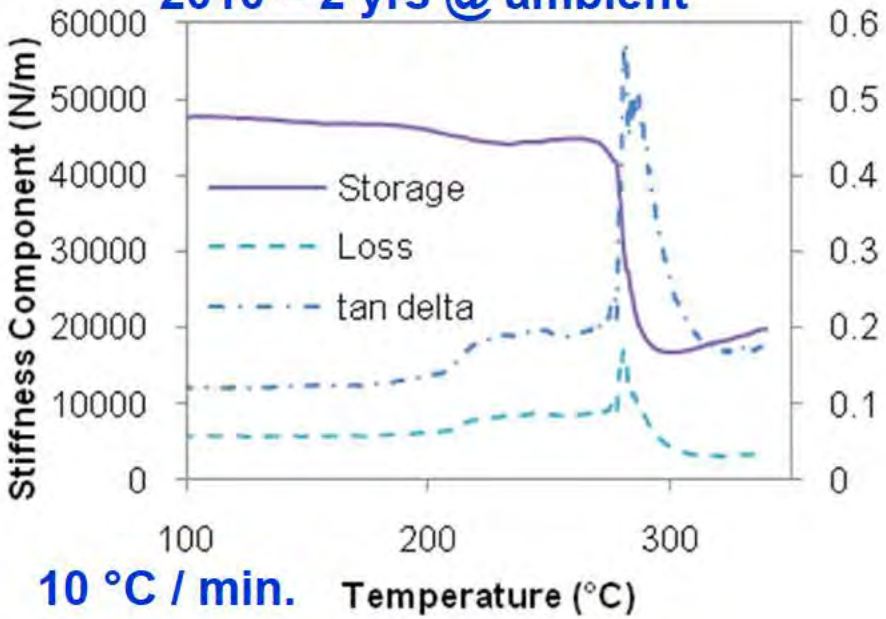


- Residual cure tends to show the universality associated with activated rate processes, which means that a change in scan rate and a shift in temperature are functionally equivalent.
- As a result, the T_G instability number tends to be insensitive to heating rate. A faster heating rate only provides a head start in the race against cure.

Even Very Rapid Scans Do Not Always Prevent *In-Situ* Cure (1)

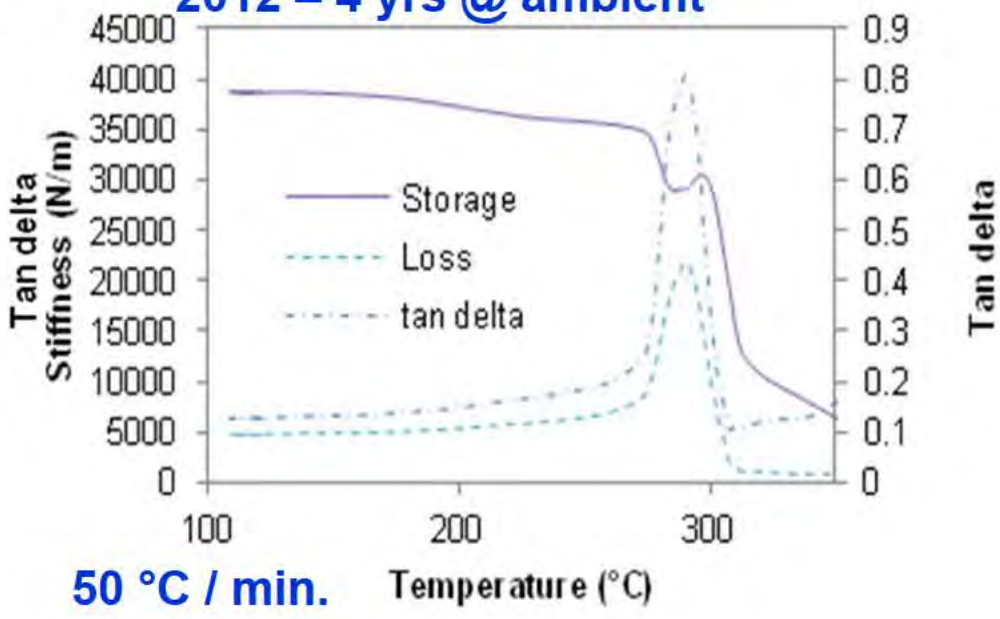
Uncatalyzed LECy (ageing study), cured at 210 °C for 24 hrs

2010 – 2 yrs @ ambient



10 °C / min.

2012 – 4 yrs @ ambient



50 °C / min.

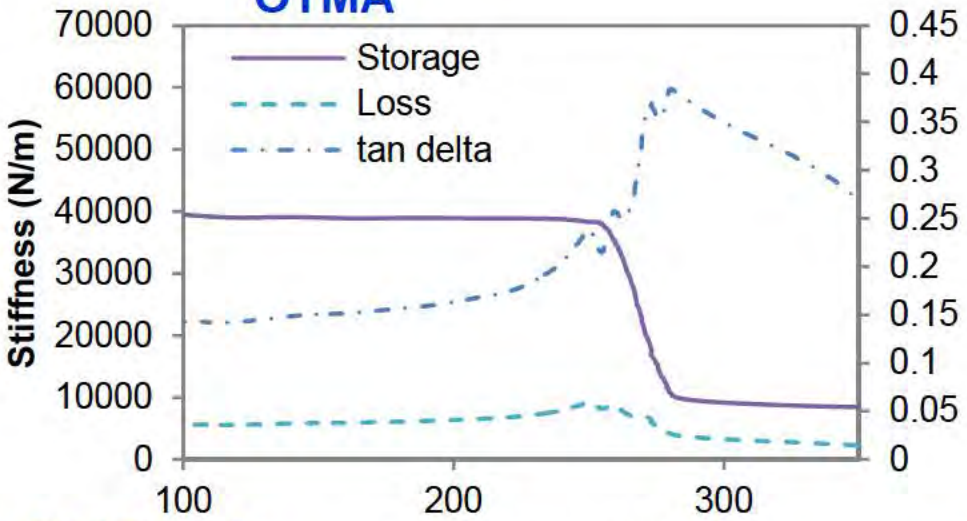
- In the 2010 sample, 10 °C / min. was a little too slow to prevent in-situ cure (the true T_G at about 240 °C) is visible as the "shoulder".
- In the 2012 sample, the true T_G is no longer discernible.

Even Very Rapid Scans Do Not Always Prevent *In-Situ* Cure (2)

Uncatalyzed LECy (unaged), cured at 210 °C for 24 hrs

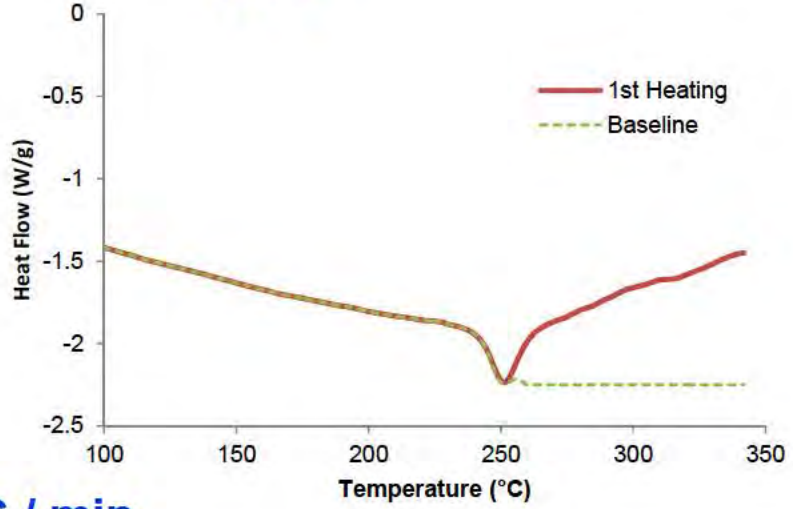
2014 – < 1 yr stored at 5 °C

OTMA



50 °C / min.

DSC

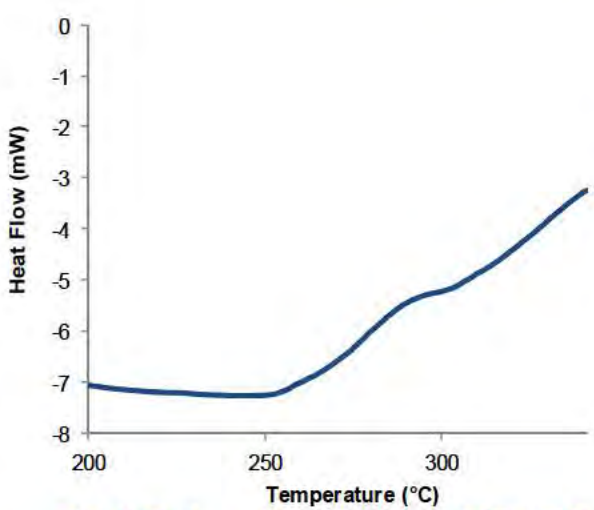


50 °C / min.

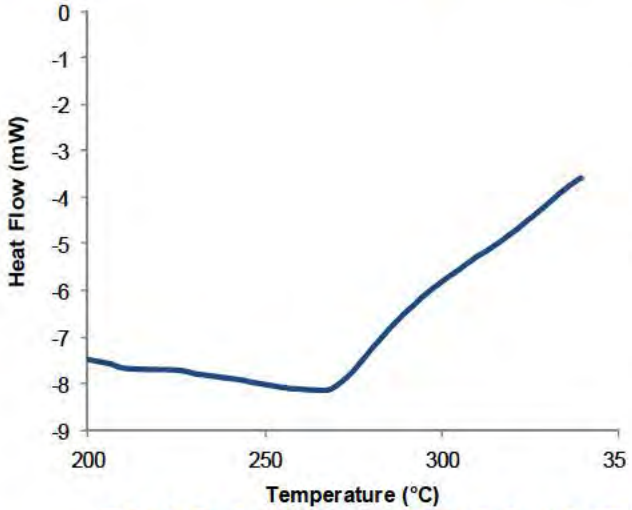
- The DSC scan shows clearly that *in-situ* cure begins immediately after passing the true T_G at about 240 °C.
- Although the loss peak in the OTMA captures the true T_G, both the storage modulus and tan delta measurements are affected by *in-situ* cure. Thus, even 50 °C/min. is only just fast enough for the OTMA scan.

A Fast DSC Scan Will Always Indicate the "As Cured" T_G

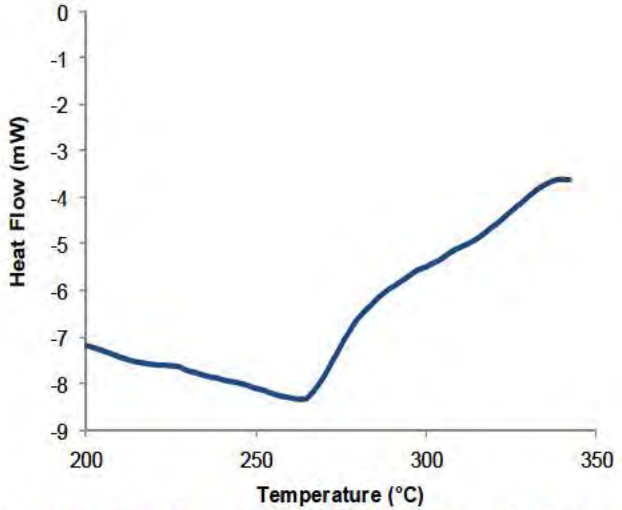
Uncatalyzed Samples; After Heating 210 °C for 24 hrs



50 °C / min. PT-30



50 °C / min. PT-30 / LECy (50/50)



50 °C / min. FlexCy/LECy (50/50)

- No cure means the T_G does not change, so the cannot have ever been in the "flat" part of the curve.
- Only a change as drastic as passing through T_G would cause such a rapid initiation of cure.
- T_G values inferred in this manner are reproducible to within 5 °C; slower heating rates work well for samples with lower values of T_G at full cure.

Summary

- In polycyanurate networks (and any other thermoset polymer network for which a single, path-independent cure mechanism exists), conversion and the glass transition temperature are intrinsically linked.
- With careful consideration of the physical properties of these networks, DSC methods can be utilized to measure conversions to within 1-2% at >80% conversion.
- Dynamic mechanical methods (especially at slow heating rates) will not measure the glass transition temperature of undercured networks correctly, due to *in-situ* cure.
- In many cases, *in-situ* cure and the resulting measurement issues cannot be avoided simply by choosing a more rapid heating rate.
- DSC methods (especially at rapid heating rates) appear to be best-suited for assessing “as cured” glass transition temperatures.


QUESTIONS?
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